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(54) Title: PHTHALATE FREE CHEMILUMINESCENT ACTIVATOR (57) Abstract There is provided a phthalate-free activator composition adapted to produce a chemiluminescent light when admixed with an oxalate solution comprising a solution of a peroxide compound in a solvent selected from acetyl trialkyl citrates, trialkyl citrates, N-alkyl-arylenesulfonamides, dialkyl adipates, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixtures thereof.		

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PHTHALATE FREE CHEMILUMINESCENT ACTIVATOR

The present invention relates to a novel chemiluminescent composition. More particularly, the present invention relates to a chemiluminescent composition having a novel activator component. Most particularly, the present invention relates to a chemiluminescent composition comprising an activator component which comprises a peroxide compound in a phthalate free solvent.

10

BACKGROUND OF THE PRESENT INVENTION

Under certain circumstances, it is desirable to have a source of visible light which is not electrically activated. Light can be provided by chemical systems, wherein the luminosity is solely the result of chemical reaction without provision of any electrical energy. Such light is known as chemiluminescent light.

Chemiluminescent light may be useful where there is no source of electricity. For example, in emergencies where sources of electrical power have failed, a chemiluminescent system could provide light. Since the system requires no externally generated source of energy, devices can be made small and highly portable. Moreover, chemiluminescent light is cold light and can be used where the heat of conventional illumination is not desired. It is also useful where electrical means could cause a fire hazard, such as in the presence of inflammable agents. Chemiluminescent light is also effective underwater since there are no electrical connections to short out. Thus it may be seen that chemiluminescent light can have many useful applications.

The production of devices capable of emitting light through chemical means is well known in the art. Lightsticks, for example, are taught in United States Patent No. 3,539,794, while other configurations have also been the subject of many United States patents, e.g., 3,749,620; 3,808,414; and 3,893,938. Additional recent patents include United States Patent Nos. 4,635,166; 4,814,949 and 5,121,302.

Typically, these devices comprise a packaging means whereby the two components of the light producing chemical reaction are kept separate until contacting of the components is desired, at which time the two components are mixed to produce chemical light by reaction. Generally the two components employed in a chemiluminescent light device are (1) a component containing a chemiluminescent compound and (2) a component containing an activator compound.

The activator containing components of the prior art typically contain a peroxide in combination with a solvent. Most commonly the solvent has comprised a phthalate such as dimethyl phthalate and dioctyl phthalate. Other prior art solvents which have been disclosed include water, alcohols, ethers such as diethyl ether, diamyl ether, tetrahydrofuran, dioxane, dibutyldiethyleneglycol, perfluoropropyl ether and 1,2-dimethoxyethane and esters such as ethyl acetate, ethyl benzoate and propyl formate. However, in order to obtain good results for peroxide stability, solubility and satisfactory light performance, phthalate type solvents are most commonly employed. See, e.g., United States Patent Nos. 4,717,511, 4,017,415, 4,698,183, and 4,508,642.

Phthalate solvents, while possessing these good characteristics, suffer from other problems that render them less attractive than in the past. It would therefore represent a significant advancement in the state of the art if another activator solvent could be found which possessed good peroxide solubility, stability and maintained good light performance. To this end, the present applicants have now found that an unexpected class of solvents provide excellent light performance characteristics and peroxide solubility, as shown in the working examples of the present application.

SUMMARY OF THE PRESENT INVENTION

According to the present invention there is provided an activator composition adapted to produce chemiluminescent light when admixed with an oxalate solution comprising a solution of a peroxide compound in a solvent selected from acetyl trialkyl citrates, trialkyl citrates, N-alkyl-arylenesulfonamides, dialkyl adipates, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixtures of any of the foregoing. The most preferred solvents are acetyl trialkyl citrates and trialkyl citrates, such as acetyl triethyl citrate and triethyl citrate.

Also according to the present invention there is provided a chemiluminescent composition comprising (a) an activator component comprising a solution of: (i) a peroxide compound; and (ii) a solvent selected from acetyl trialkyl citrates, trialkyl citrates, N-alkyl-arylenesulfonamides, dialkyl adipates, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixtures of any of the foregoing; and, optionally, (iii) a catalyst; and (b) a chemiluminescent component comprising (i) a bis-ester of oxalic acid; and (ii) an organic fluorescent compound.

Still further, according to the present invention there is provided a chemiluminescent device comprising (1) a first section containing a solution of a peroxide compound in a solvent selected from acetyl
5 trialkyl citrates, trialkyl citrates, N-alkyl-arylenesulfonamides, dialkyl adipates, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixtures of any of the foregoing, and optionally a catalyst; (2) a second section containing a chemiluminescent component
10 comprising (i) a bis-ester of oxalic acid; and (ii) an organic fluorescent compound; and (3) a rupturable separation means for separating said first and second sections and which ruptures upon application of pressure to allow contact of the components contained in said
15 first and second sections.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention provides a novel phthalate free activator component for use in chemiluminescent light producing systems. The novel
20 phthalate free activator components employ solvents which are possessed of good peroxide solubility, stability and light performance characteristics.

The peroxides employed in the activator components of the present invention may be any
25 hydroperoxide compound. Typical hydroperoxides include t-butylhydroperoxide, peroxybenzoic acid and hydrogen peroxide. Hydrogen peroxide is the preferred hydroperoxide and may be employed in the anhydrous form such as perhydrate of urea (urea peroxide), perhydrate of
30 pyrophosphate (sodium pyrophosphate peroxide), perhydrate of histidine (histidine peroxide), sodium perhydrate of pyrophosphate (sodium pyrophosphate peroxide), sodium

perborate, sodium peroxide. and the like. Whenever hydrogen peroxide is contemplated to be employed, any suitable compound may be substituted which will produce hydrogen peroxide.

5 The activator solvents of the present invention are those which are phthalate free and which provide good solubility and stability with the peroxide. In the broadest terms these compounds include plasticizers such as trialkyl citrates, acetyl trialkyl citrates, dialkyl
10 adipates, alkyl-substituted arylenesulfonamides, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixtures thereof. More particularly they include, but are not limited to, triethyl citrate, diisobutyl adipate, acetyl triethyl citrate, N-ethyl-o,p-toluenesulfonamide,
15 acetyl tributyl citrate and mixtures thereof. Particularly suitable for use in the practice of the present invention are triethyl citrate, acetyl triethyl citrate and mixtures thereof.

 The peroxide and solvent are combined to form
20 the activator solutions of the present invention. Preferably the hydrogen peroxide concentration in the activator solution ranges from about 0.2M to about 15M.

 Optionally, the activator solutions of the present invention may further comprise catalysts, as is
25 known to those of ordinary skill in the art. Typically, the catalysts are those which are weakly basic such as sodium salicylate and tetrabutylammonium salicylate, etc. See, United States Patent No. 3,775,336. Other useful catalysts include lithium salicylate, potassium
30 salicylate, rubidium chloride, lithium chloride, lithium sulfate and tetrabutylammonium perchlorate. See, United States Patent No. 3,704,231. Particularly useful in the practice of the present invention is sodium salicylate. It is further contemplated by the present invention that
35 the catalyst may be contained in the chemiluminescent component instead of the activator component.

In preparing the chemiluminescent compositions of the present invention it is necessary to contact the activator solution with a component containing a chemiluminescent compound.

5 Useful chemiluminescent compounds are selected from 3-aminophthalhydrazide, 2,4,5-triphenylimidazole, 10,10'-dialkyl-9,9'-biacridinium salts, 9-chlorocarbonyl-10-methylacridinium chloride, and bis(substituted-phenyl)oxalate, bis(2-nitrophenyl)oxalate, bis(2,4-10 dinitrophenyl)oxalates. Other useful oxalate compounds include those such as bis(2,6-dichloro-4-nitrophenyl)-oxalate, bis(2,4,6-trichlorophenyl)oxalate, bis(3-trifluoromethyl-4-nitrophenyl)oxalate, bis(2-methyl-4,6-15 dinitrophenyl)oxalate, bis(2,4-dichlorophenyl)oxalate, bis(2,5-dinitrophenyl)oxalate, bis(2-formyl-4-nitrophenyl)oxalate, bis(pentachlorophenyl)oxalate, bis(1,2-dihydro-2-oxo-1-pyridyl) glyoxal, bis-N-phthalimidyl oxalate, bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate, bis(2,4,5-trichloro-6-carbobutoxyphenyl) 20 oxalate, and bis(2,4,6-trichlorophenyl)oxalate, and mixtures thereof.

A fluorescent compound is also typically employed in the chemiluminescent components of the present invention for light emission purposes. 25 Fluorescent compounds for use with the oxalic-type chemiluminescent compounds should be soluble in the chemiluminescent component solvent, if any, at least to the extent of 0.0001 moles per liter.

Typical suitable fluorescent compounds for use 30 in the present invention are those which have a spectral emission falling between 330 millimicrons and 1000 millimicrons. Among these are the conjugated polycyclic aromatic compounds having at least 3 fused rings, such as anthracene, substituted anthracene, benzanthracene,

phenanthrene, substituted phenanthrene, naphthacene, substituted naphthacene, pentacene, substituted pentacene, and the like. Typical substituents for all of these are phenyl, phenylethynyl, lower alkyl, chlorine, bromine, cyano, alkoxy (C_1-C_{16}) and other like substituents which do not interfere with the light-generating reaction contemplated herein.

Numerous other fluorescent compounds having the properties given hereinabove are well known in the art. Many of these are fully described in Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, NY 1949. Other useful fluorescers are described in Berlman, "The Handbook of Fluorescence Spectra of Aromatic Molecules," 2d. ed., Academic Press, New York, NY 1971.

The oxalate compound and fluorescent compound are generally diluted in a suitable solvent or diluent. Typical diluents or solvents which can be used for the oxalate component are esters such as ethyl acetate, ethyl benzoate, butyl benzoate, dimethyl phthalate, dibutyl phthalate, dioctyl phthalate, methyl formate, triacetin, diethyloxalate and dioctyl terephthalate; aromatic hydrocarbons such as benzene, toluene, ethyl benzene, butyl benzene; and chlorinated hydrocarbons such as chlorobenzene, chloroform and carbon tetrachloride. Preferred are butyl benzoate, dibutyl phthalate and dimethyl phthalate. However, in some embodiments it is preferred to employ a non-phthalate solvent for the oxalate component in order to provide a completely phthalate free chemiluminescent device.

The chemiluminescent devices can then be prepared according to the teachings of the prior art. Generally, the activator component is placed in a first section of the device and the chemiluminescent component
5 in a second section of the device. The two sections are separated by a rupturable separation means such as an ampoule or a wall. Upon application of a desired amount of pressure, the separation means ruptures or opens to allow the activator component to come into contact with
10 the chemiluminescent component, thereby causing a chemiluminescent reaction and the production of light.

In the case of the use of an ampoule, it is contemplated by the present invention that either the activator component or the chemiluminescent component may
15 be placed inside the ampoule.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples illustrate the present invention. They are not to be construed to limit the scope of the appended claims in any manner whatsoever.

20

EXAMPLES 1-7

Various activator solutions are prepared by dissolving 2.3 weight percent peroxide, 9.0 weight percent t-butyl alcohol and 0.095% sodium salicylate in 88.605 weight percent solvent. The solutions are then
25 heat treated by aging at 65°C for 15 days. The results, along with compositional data are set forth below in Table 1.

TABLE 1

Example	Solvent	Original % H ₂ O ₂	Aged % H ₂ O ₂	Percent Loss	Comments
A*	Dimethyl Phthalate	2.29	2.25	2.0	Control example.
1	Triethyl Citrate	2.29	2.25	2.0	Good light performance initially and after accelerated aging.
2	Diisobutyl adipate	2.30	1.99	13.0	Good light performance initially and after accelerated aging. Good high intensity light.
3	Acetyltriethyl citrate	2.32	2.11	10.0	Good light performance initially and after accelerated aging.
4	Pentaerythritol tetrabenzoate	a	a	a	Solid at room temperature. Fair light performance.
5	N-ethyl-o,p-toluene-sulfonamide	2.20	1.67	24.0	Poor light performance.
6	Glyceryltribenzoate	2.20	1.70	23.0	Solid at room temperature. Fair light performance. Difficulty analyzing for peroxide.
7	Acetyltributyl citrate	2.20	1.22	45.0	Good light performance initially but poor performance after accelerated aging.
B*	Butyl Benzoate	2.30	0.20	92.0	Peroxide unstable and not completely soluble. Solvent migrates through the polyethylene casing in storage.

* = Comparative Example

It can be seen from the data above that all of these non-phthalate solvents except butyl benzoate can be utilized in chemiluminescent products. The solvents may be used in a variety of product formats including reverse (oxalate in ampoule), double reverse (catalyst and oxalate in ampoule) and frozen (pentaerythritol tetrabenzoate and glyceryl tribenzoate).

EXAMPLE 8

An activator solution employing triethyl citrate as solvent is compared with an activator solution employing dimethyl phthalate as solvent in a six-inch green lightstick containing 5.6 grams of the respective activator solutions.

The oxalate component consisted of a 5.0 gram ampoule containing 14.0 weight percent bis(2,4,5-trichloro-6-carbopentoxyphenyl)oxalate (CPPO), 0.17 weight percent 2-methyl-9,10-bis(phenylethynyl)-anthracene (MBPEA) fluorescer and the rest butyl benzoate solvent.

The light output was measured over time at 75°F ± 2°F with a Tektronix J-16 Light Meter with J-6501 Illuminance Probe positioned 1.5 inches from lightstick.

The results along with compositional data are set forth below in Table 2.

TABLE 2

<u>Example</u>	<u>8A*</u>	<u>8</u>
Composition, wt. %		
H ₂ O ^a	2.3	1.5
tBA ^a	9	6
DMP ^b	rest	--
Triethyl citrate	--	rest
NaSal ^c	0.0095	0.006
Light Output, lux		
5 min	50.5	32.8
10	44.5	37.3
15	41.8	38.9
20	38.7	38.9
30	32.5	34.6
1 hr	21.8	24.8
2	10.8	13.6
3	6.7	8.9
4	5.5	4.5
5	2.9	2.9
6	1.9	2.1
7	1.2	1.4
8	0.81	0.90
9	0.66	0.75
10	0.53	0.61

* = Comparative example
 a = t-butyl alcohol diluent
 b = dimethyl phthalate solvent
 c = sodium salicylate catalyst

From the data set forth in Table 2 it can be seen that the triethyl citrate activator provides excellent light output characteristics. Note that the light performance for triethyl citrate activator is better in the 1 to 3 hour period than the dimethyl phthalate making the triethyl citrate activator more advantageous as a solvent in certain products.

EXAMPLE 9

An activator solution employing triethyl citrate as solvent is compared with an activator solution employing dimethyl phthalate as solvent in a four-inch green lightstick containing 1.70 grams of the respective activator solutions.

The oxalate component consisted of a 2.4 gram ampoule containing 14.0 weight percent bis(2,4,5-trichloro-6-carbopentoxyphehyl)oxalate (CPPO), 0.17 weight percent 2-methyl-9,10-bis(phenylethynyl)-anthracene (MBPEA) fluorescer and the rest butyl benzoate solvent.

The light output was measured over time at 75°F ± 2°F with a Tektronix J-16 Light Meter with J-6501 Illuminance Probe positioned 1.5 inches from lightstick.

The results along with compositional data are set forth below in Table 3.

TABLE 3

<u>Example</u>	<u>9A*</u>	<u>9</u>
<u>Composition, wt. %</u>		
H ₂ O _a	2.3	1.5
tBA _b	9	6
DMP _b	rest	--
Triethyl citrate	--	rest
NaSal ^c	0.0095	0.006
<u>Light Output, lux</u>		
5 min	23.4	16.0
10	21.3	15.3
15	19.5	14.9
30	17.9	15.4
1 hr	14.9	14.7
2	9.5	11.4
3	6.0	8.2
4	3.6	5.7
5	2.4	4.0
6	1.7	2.7
7	1.1	1.8
8	0.85	1.3
9	0.63	0.94
10	0.47	0.70
11	0.36	0.46
12	0.28	0.37

* = Comparative example
 a = t-butyl alcohol diluent
 b = dimethyl phthalate solvent
 c = sodium salicylate catalyst

The data presented in Table 3 show the excellent results obtained with the triethyl citrate solvent activator in comparison with the dimethyl phthalate solvent activator. The significant improvement
5 in light performance at 2 hours and beyond makes the activators of the present invention uniquely suitable for many applications which are not possible with the phthalate solvents.

The above mentioned patents are hereby
10 incorporated by reference.

Many variations of the present invention will suggest themselves to those skilled in the art in light of the above-detailed description. For example, any of the trialkyl citrates or acetyl trialkyl citrates may be
15 employed as the solvent for the activator component. Further, a wide variety of fluorescers and oxalates may be employed in the chemiluminescent component. All such obvious modifications are within the full intended scope of the appended claims.

CLAIMS

1. A phthalate-free activator composition adapted to produce a chemiluminescent light when admixed with an oxalate solution comprising a solution of a peroxide compound in a solvent selected from acetyl
5 trialkyl citrates, trialkyl citrates, N-alkyl-arylenesulfonamides, dialkyl adipates, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixture of any of the foregoing.

2. An activator composition as defined in Claim 1 wherein said peroxide compound comprises hydrogen peroxide.

3. An activator composition as defined in Claim 1 wherein said solvent is selected from triethyl citrate, acetyl triethyl citrate, tributyl citrate, acetyl tributyl citrate, N-ethyl-o,p-toluenesulfonamide,
5 diisobutyl adipate and mixtures of any of the foregoing.

4. An activator composition as defined in Claim 3 wherein said solvent comprises triethyl citrate.

5. An activator composition as defined in Claim 1 wherein said peroxide compound comprises hydrogen peroxide and said solvent comprises triethyl citrate.

6. A chemiluminescent composition comprising
(a) an activator component comprising a solution of:

(i) a peroxide compound;

(ii) a solvent selected from acetyl trialkyl
5 citrates, trialkyl citrates, N-alkyl-arylenesulfonamides, dialkyl adipates, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixtures of any of the foregoing; and, optionally,

(iii) a catalyst; and

10 (b) a chemiluminescent component comprising

(i) a bis-ester of oxalic acid; and

(ii) an organic fluorescent compound.

7. A chemiluminescent composition as defined in Claim 6 wherein said peroxide compound (a)(i) comprises hydrogen peroxide.

8. An activator composition as defined in Claim 6 wherein said solvent is selected from triethyl citrate, acetyl triethyl citrate, tributyl citrate, acetyl tributyl citrate, N-ethyl-o,p-toluenesulfonamide,
5 diisobutyl adipate and mixtures of any of the foregoing.

9. An activator composition as defined in Claim 8 wherein said solvent comprises triethyl citrate.

10. A chemiluminescent device comprising

(1) a first section containing a solution comprising a peroxide compound in a solvent selected from acetyl trialkyl citrates, trialkyl citrates, N-alkyl-
5 arylenesulfonamides, dialkyl adipates, pentaerythritol tetrabenzoate, glyceryl tribenzoate and mixture of any of the foregoing; and

(2) a second section containing a chemiluminescent component comprising (i) a bis-ester of
10 oxalic acid; and (ii) an organic fluorescent compound; and

(3) a rupturable separation means for separating said first and second sections and which ruptures upon application of pressure to allow contact of
15 the components contained in said first and second sections.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/01888

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : CO9K 3/00; F21K 2/00

US CL : 252/700; 362/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/582, 700; 362/34

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS TEXT SEARCH FOR CHEMILUMINESCENCE and various solvents of claims.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,508,642 (WORLD) 02 April 1985. See Table D and claims	1-10
X	US,A, 3,888,786 (MAULDING) 10 June 1975. See column 3, lines 53-62	1, 2, 6, 7
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Y		3, 8, 10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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